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A R T I C U L O

Structural evolution of the SiO_2-Ag system prepared by the Sol-gel process with incorporation of Ag particles

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Structural evolution of Sol-Gel glasses in powder form and coatings with incorporation of Ag particles at the starting solution showed an evolution from SiO_2 amorphous matrix to the cristobalite phase with the annealing treatment at around 800 ºC for one hour. This structural evolution was obtained at lower Ag concentration up 0.7 %vol. Two series of samples were studied, A) series using HNO_3 and B) series using HCl as catalytic agent; in both series grenetine was used as a dispersing agent to avoid the precipitation of Ag particles. We found the incorporation of silver in the xerogeles matrix promotes the devitrification process at relatively low temperatures with the presence of partial crystallization in form of cistobalite. This structure was produced by controlling the catalytic agent quoted in the preparation process. The EPR and UV-Vis absorption spectra show the presence of Fe^{3+} ions as a contaminant in the source of the Ag particles, due to the process to obtain these particles. By means the IR spectra a high (OH^-) concentration at higher temperatures was observed in this system, until 600 ºC at difference of the sol-gel glasses made with incorporation of Ag particles by nitrates. The color evolution of the coating samples with the annealing temperature varies from a light brown at 100 ºC to yellow at 500 ºC.

Keywords: sol-gel, Ag particles, cristobalite

Evolución estructural del sistema SiO_2-Ag preparado por el proceso Sol-Gel con incorporación de partículas de Ag.

La evolución estructural de vidrios de Sol-Gel en forma de polvos y recubrimientos preparados con la incorporación de partículas de Ag a partir de la solución precursora muestra la evolución de la matriz amorfa de SiO_2 a la fase cristobalita utilizando tratamientos térmicos alrededor de 800 °C por un tiempo de una hora. Dicha evolución estructural fue obtenida en concentraciones bajas a partir de 0.7% de Ag. Dos series de muestras fueron estudiadas, la serie A) usando HNO_3 y la serie B) usando HCl como agente catalítico; en ambas series se uso grenetina como agente dispersante para evitar la precipitación de las partículas de Ag. Nosotros encontramos que la incorporación de plata en la matriz de los xerogeles promueve el proceso de desvitrificación a temperaturas relativamente bajas con la presencia de una cristalización parcial en forma de cristobalita. Esta estructura fue producida controlando el agente catalítico mencionado en el proceso de preparación. Los espectros de EPR y absorción UV-Vis muestran la presencia de iones Fe^{3+} como un contaminante proveniente de las partículas de Ag, debido al proceso en el que fueron obtenidas las partículas. Por medio de espectroscopía IR se observo que en el sistema hay una alta concentración de (OH^-) a temperaturas altas, hasta 600 ºC a diferencia de los vidrios producidos por sol-gel con la incorporación de partículas de Ag en forma de nitratos. La evolución del color en muestras con el recubrimiento con el tratamiento térmico varía de café ligero a 100 ºC hasta amarillo a 500 ºC.

Palabras claves: sol-gel, partículas Ag, cristobalita

1. INTRODUCTION

The incorporation of particles in the sol-gel glasses has shown a great variety of properties [1, 2, 3, 4, 5] in bulk and coating samples. The incorporation of some kind of particles has a strong influence in the evolution structure of the glass. Sol-gel chemistry and further processing to xerogeles allow flexibility in obtaining a great variety of materials based on incorporation of particles embedded in inert materials such as SiO_2 with specific properties, which are related to the structure of the final materials. These materials have also been used experimentally as supporting substrates for molecular chemical systems and for artificial photosynthesis, including organic photoactive or electroactive molecules which has opened new opportunities for optical and electrooptical applications. This is, since its inception decades ago, sol-gel encapsulation has opened up an intriguing new way to immobilize biological materials. The advantages of these living ceramics might give then applications as optical end electrochemical sensors, diagnostic devices, catalyst and even

bioartificial organs. With advances in sol-gel precursors, nano engineered polymers, fabrication methods, this technologies promise to revolutionize bioimmobilizations.

The crystallization of silica glasses has been investigated since shortly after the discovery of glass. The rate and mechanism of crystallization vary with the chemical composition of the glass, temperature and atmosphere. It has been observed that the presence of alkali metal, water and oxygen accelerates the crystallization rate of glass [6,7].

It is well known that mixtures of silica gel and several metal oxides annealed at temperatures within the range of 500 to 1200 ºC produce crystallization of the amorphous SiO_2 into the quartz and cristobalite phases [8]. For example: when mixtures of silica gel with additives such as Li_2CO_3, MgO, $CaCO_3$, SrO, $Ba(CH_3COO)_2$ and ZnO annealed at temperatures from 700 to 1050 ºC, quartz was obtained. The formation of quartz was closely related to the presence of a metal silicate. In a previous report of Takeuchi *et. al*. [8]. It was assumed that this metal silicate in contact with silica gel promoted the quartz nucleation.

In the same way recently our research group has reported the crystallization of SiO_2 sol-gel made with the introduction of the metal nitrates in the starting solution, Ag, Cu and mixtures of Ag and Cu [9,10,11,12] obtaining low temperatures of crystallization, 600 ºC for quartz in the mixture with $AgNO_3$ and ($Cu(NO_3)_2$) and 500 ºC for the α-cristobalite with the introduction of $AgNO_3$.

Two possible mechanisms which could explain the crystallization are: 1) the influence of metal incorporation at low temperature crystallization, in sol-gel glasses and for that to occur, metal needs to be added in amounts such as to form crystalline aggregates and 2) the SiO_2 samples must be prepared from precursor solutions with high H_2O/TEOS ratios and the samples need be in bulk form. Also results indicate that in coating form samples annealed to 800 ºC the crystallization process was not observed.

On the other hand, several reports [13,14,15,16] on different kind of glasses with incorporation of Ag by melting and some other glasses prepared by the sol-gel route, only the nucleation kinetics and growth of the Ag particles were observed; however, the glass structure was not affected, that is, some kind of the SiO_2 crystallizations, never observed. Sol-gel a low temperature process, also provides easy control of silver concentration and the possibility of adding reducing and oxidizing agents in small concentrations to modify the chemical state of silver. The goal of these modifications at ion metal is due to some recent works report preparation and physical properties of silica containing different amounts of silver in various chemical states by the sol-gel method, both in powder and coating form. However, little attention has been paid to understanding the effects of microstructural properties of the silica matrix and its effect on the formation of silver particles. Actually, silver doped glassy silica is used in several biotechnological applications, such as, antimicrobial agents and optical filters [17,18,19]. Nevertheless, it is necessary to realize more studies to understand the mechanisms by which better physical properties of these new materials can be obtained. With these facts in mind, in this work was explored the influence of metal Ag particles incorporation in the starting solution of the SiO_2 sol-gel glasses and annealing was explored at temperatures from 100 up to 800 ºC, on the structural evolution of the SiO_2 matrix.

2. EXPERIMENTAL DETAILS

2.1 Sample preparation

Powder and coating samples, with different silver particles concentrations, were prepared using the traditional sol-gel method. The sol-gel precursor solution was obtained mixing tetraethyl orthosilicate (TEOS) (Baker, 98%) and ethanol with a molar ratio ethanol to TEOS of 4. The molar ratio water to TEOS was of 11.7.

The Ag was added to the starting solutions using particles of Ag with an average size 4.7 μm previously prepared, in a 0.2679 *M* solution of $AgNO_3$ that contained an oxidizing agent. An iron electrode was introduced into the solution to start the cementation reaction between the silver ion and the iron electrode. The reaction between the solution and the electrode produced the Ag particles; this reaction was strongly accelerated with the presence of the oxidizing agent added in small quantities. Silver powder was separated by sedimentation; it was then rinsed with enough water to eliminate the excess of catalyst and hydrated iron oxide. Following that, the silver powder was sedimented from the aqueous suspension; the water excess was removed by decantation and the powder dried in an oven obtaining Ag particles with diameter sizes between 400 and 650 nm with the maximum centred around 470 nm. More details about the process have been reported elsewhere [20]. The Ag particles were dispersed in the solution adding a small quantity of grenetine (0.2 mg) to avoid Ag precipitation. To prepare the solutions: first, the TEOS was mixed with ethanol using a magnetic stirrer for 15 minutes. In a separate vessel, the silver particles joined to the grenetine were dissolved in distilled water and then added to the TEOS-ethanol solution to form the precursor solution in order, to prepare the coating and powders samples.

Samples with different silver concentrations were obtained by varying the amount of Ag particles in the starting solution. Considering that all silver added to the solution are in the form of metallic Ag particles, the nominal amount of silver in the final glass was 0.3, 0.7, 2 and 4 %vol. To catalyze the hydrolysis and condensation reactions, nitric acid (series samples A) and chloride acid (series samples B) were added in small quantities. The two different series samples were labeled A and B respectively. The coatings were deposited on commercial corning glass slides. To obtain the coatings, the substrates were immersed in the starting solutions when said solution had a viscosity of approximately 3 mPa.s. After being kept in the solutions for a few seconds, they were removed at a constant speed of 3.2 mm/sec. Under these conditions, the coatings had an uniform thickness of about 0.5 μm. The film thickness was measured using Kektalk II surface profile equipment. Immediately after preparation, the coatings were dried in a conventional oven at 100 ºC for 10 min using an atmospheric oxygen, that was, at room temperature.

The powder samples were obtained by drying the same starting solutions at 100 ºC for 3.5 hr. Additional thermal air treatments were done at 300, 500, 600 and 800 ºC for the powder samples for 1 hour. Also, to avoid the softening of the glass slides, the coatings were only annealed at 300 and 500 ºC during 1 hour.

2.2 Experimental techniques

The materials prepared were characterized using X-ray diffraction (XRD), electron paramagnetic resonance (EPR) and optical measurements.

The XRD measurement on powder samples was obtained in a Rigaku difractometer D/Max-2100, using CuK_α radiation, operating at 30KV and 16 mA. The powder patterns were obtained using the θ-2θ standard mode. All patterns were recorded in the range of 15 to 80 degrees on the 2θ scale. For the characterization of the microstructure samples, the modified Warren-Averbach (WA) method was employed [21]. By this method the line profile of the diffraction peaks was analyzed, which allows obtained estimates of 2θ angular positions of both Ag and cristobalite phases and the crystalline grain size of the samples. The EPR spectras were obtained by means of X-band using a Jeol JES-3RX EPR spectrometer with 100 kHz magnetic field modulation. The measurements were performed on powder samples at room temperature and 77 K (-196 °C).

UV-Vis absorption measurements on coating were made using a PERKIN ELMER UV/VIS Spectrophotometer Lambda 2 and diffuse reflectance measurements on powder were made on an Ocean Optics Inc. SD2000 fiber optic spectrometer. Infrared spectroscopy measurements on powder were made on a Nicolet Avantar 360 FT-IR spectrometer operating in the diffuse reflectance mode.

3. EXPERIMENTAL AND DISCUSSION RESULTS

Fig. 1 shows the diffraction pattern in powder samples with 2 %vol. of Ag, with different catalyzes. Fig. 1 A) and corresponds to the samples prepared with HNO_3 and the Fig B) correspond to the samples prepared with HCl. The patterns show the evolution samples with the annealing temperature from 100 to 800 ºC. Both series of samples showed the presence of the Ag particles at 100 ºC and transformations were observed from the amorphous phase of the SiO_2 to α-cristobalite phase at around 800 ºC. Similar behavior was observed for samples with 0.7 and 4 %vol. of Ag.

Fig. 2 shows the evolution pattern of the X-Ray diffraction for samples prepared using A) HNO_3 and B) HCl at annealing temperature of 800 ºC with different Ag concentration. From this figure, it was observed that the introduction of Ag particles in the sol-gel system treated at this annealing temperature induced the formation of the α-cristobalite phase up to 0.7 %vol. of Ag. At lower Ag concentrations there the presence of α-cristobalite was not observed.

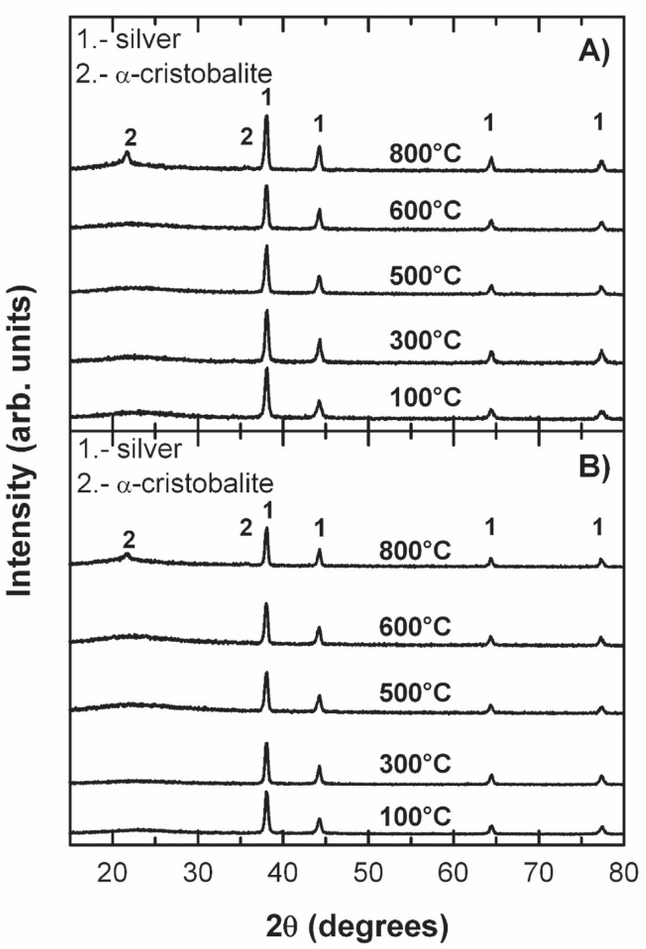

Fig. 1. XRD patterns in powder of the samples with 2 %vol. of Ag, using two different catalyzes, A) HNO_3 and B) HCl.

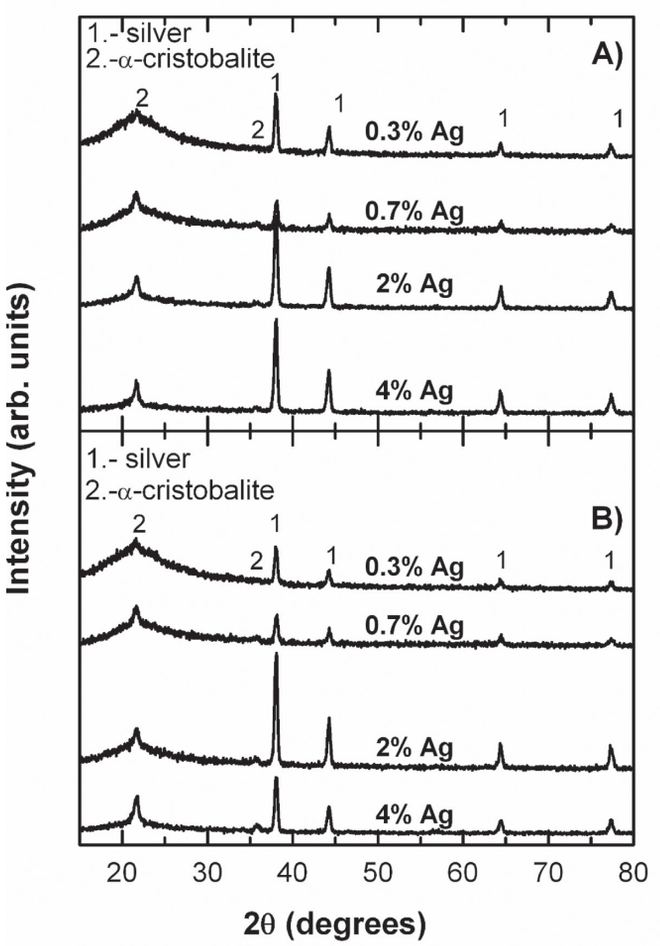

Fig. 2. Pattern of the X-Ray diffaction for samples prepared using A) HNO_3 and B) HCl; at annealing temperature 800ºC with different Ag concentration.

Fig. 3 shows the data of the crystalline grain size for samples with 0.3, 0.7, 2 and 4 %vol. of Ag annealed at 800 ºC, and samples with 2%vol of Ag annealed at 100, 300, 500, 600 and 800 ºC, respectively. These samples were obtained at different catalyzes: HCl and HNO_3. The crystalline grain size was obtaining using the Warren-Averbach method analyzing the line profile of the diffraction peaks. In general it has been observed that the estimated size of the Ag particles for samples with HCl was lower than in the HNO_3 case, independent of the annealing temperature. A similar behavior was observed in the Ag particles size as a function of the silver concentration. Notice that this result does not depend either on the annealed treatment or the silver concentration incorporate to the starting suspension. The grain size of the α-cristobalite phase was around 4 nm for both series of samples.

Fig. 4 shows the evolution of the absorption spectra of powders samples for the A) and B) series obtained by diffuse reflectance. For both series a similar behavior was observed of the absorption spectra because at 800 ºC the spectrum shows a well resolved band at around 390 nm associated with Ag particles of nanometric size, this band was best resolved in the series B) case at the same temperature. The color evolution of the samples A) varied from at brown dark color at lower annealing temperature to a yellow-brown color at 800 ºC. The samples B) were more transparent; at lower temperatures they were brown, and yellow at 800 ºC. By the evolution of spectra as a function of the annealing temperature, it was inferred there exists a migration process of atomic Ag in the SiO_2 with the thermal treatment to form nanometric Ag particles and a medium with a more homogeneous refractive index at higher annealing temperatures.

Fig. 5 shows absorption spectra of coating samples for B series. For annealed temperatures of 100, 300 and 500 ºC the samples show a lower background absorption in visible ranges. At 500 ºC there was a significant change in the absorption spectrum, because the characteristic absorption band due to Ag colloidal particles giving way to a semitransparent yellow color of the coating is well resolved. This effect was not observed in the case of the coating samples for A series, in fact these coating samples only show a higher background absorption in visible ranges, that was increased with the annealing treatment, but reaching 500 ºC it. The band absorption of the Ag colloidal particles was not observed, this appreciable difference behavior was pointed in the absorption spectra of the powder samples by diffuse reflectance.

Typical IR data, in the range of 400 to 1700 cm^{-1}, are shown in Fig. 6 for samples of A and B series as a function of the annealing temperature. In this Figure we identified at 450 y 800 cm^{-1} corresponding to rocking (R) and bending (B) modes, respectively, while in the range of 1000-1300 cm^{-1} corresponds to vibration in the amorphous SiO_2 network and were associated with the bending and asymmetric stretching of the Si-O-Si bonds, respectively [22]. The latter band is related to the asymmetric mode AS_1 located in the range of 1081-1112 cm^{-1} and the coupled disorder induced AS_2 mode at 1190 cm^{-1}. It is observed that the AS_1 band shifts to a higher position suffering a slight broadening, which indicates a more ordered SiO_2 amorphous structure. The band at 960 cm^{-1} reveals the Si-OH groups characteristic of sol-gel materials, attained to the pore walls[23, 24].Water molecules by the bending mode are identified by the bands at 1690 cm^{-1}, which band at 600ºC was appreciably reduced. The band associated with Si-OH group disappeared totally at 800 ºC and at this temperature the small additional band at around 617 cm^{-1} associated with

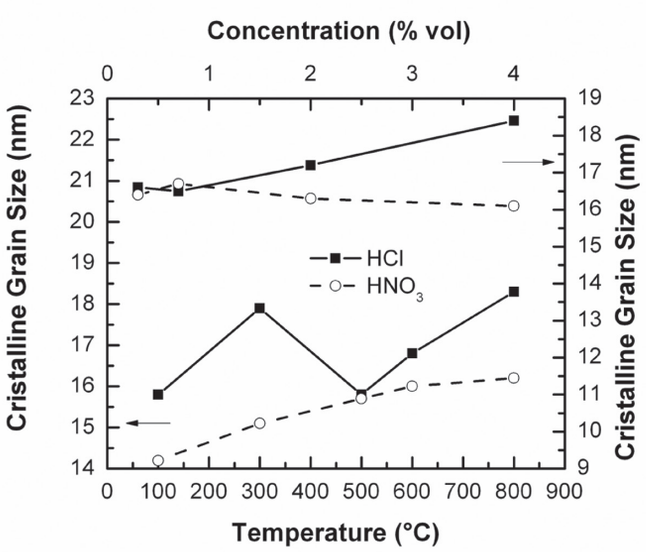

Fig. 3. The crystalline grain size for samples with 0.3, 0.7, 2 and 4 %vol. of Ag and samples annealed at 100, 300, 500, 600 and 800 ºC, respectively

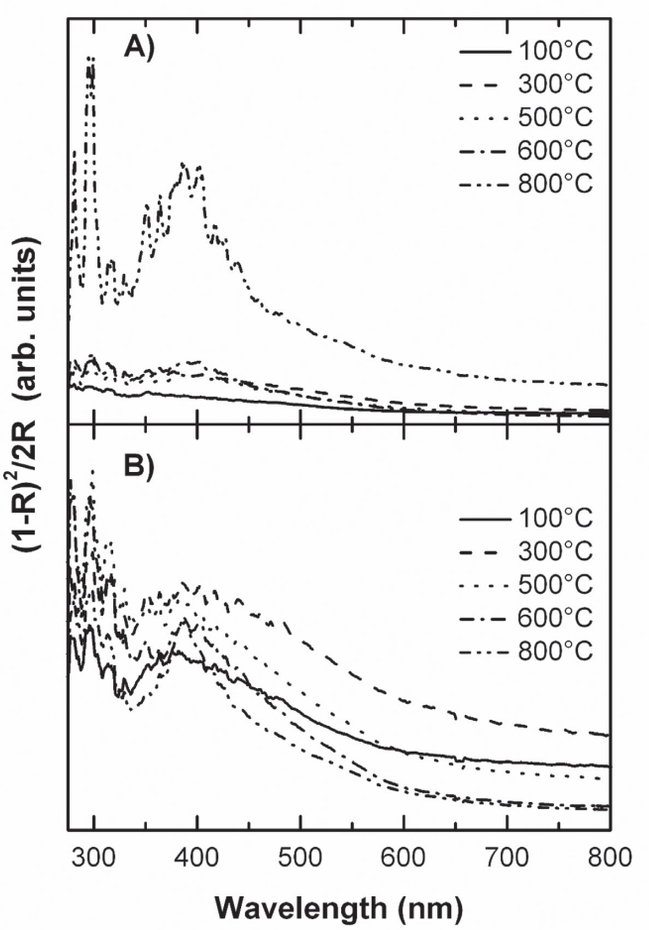

Fig. 4. Shows the evolution of the absorption spectra of powders samples for the A) and B) series obtained by diffuse reflectance.

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the α-cristobalite phase of the SiO_2 was observed. Similar behavior was observed in both series of samples except that the elimination of OH groups is at lower temperatures in the B samples (samples catalyzed with HCl). The existence of OH group at around 3500 cm^{-1} up temperatures of 600 ºC must be pointed.

Fig. 7 shows the EPR spectra evolution with the annealing temperature for the series of samples A and B. In both series a drastic evolution with the thermal treatment was observed. At 100 ºC was observed a hyperfine structure around 3.4 KOe with six lines in both samples A and B. This hyperfine structure observed in both series of samples at 100 ˚C in accordance with the literature may be associated with the conformation of complex entities with Ag, Cl, NO_3, amines groups and carboxyl groups. This kind of spectra, then was probably the result of interaction between two Cl^- neighbors giving place to the superhyperfine structure [25]., additionally in this region Swarnabala *et al.* working with 2-aminomethylpyridine-silver nitrate we found a superhyperfine structure due to the interaction of two $^{14}N(I=1)$ [26].. This fact is supported by the evidence that the catalytic agents (HNO_3 and HCl) produce dissolution of the Ag particles, resulting AgCl and another complex with the grenetine. Additionally a structure around 1.6 KOe and 3.3 KOe and broad resonance line around 3 KOe, were absorbed at 800 ˚C; in both series of samples this structure was similar to the Fe^{3+} ions in octahedral symmetry in SiO_2 [27, 28].. This structure was best resolved at 300 ºC for samples with HCl. In the HNO_3 at 300 ºC the presence of a sharp line around 3.4 KOe probably due to a radical of the type O_2^- and OH^- [29], is observed. For T=500 ºC EPR spectrum shows a single broad line around 3 KOe, this broad resonance line, has the characteristic form of a particles system with strong dipolar interaction. Said interaction among the Ag particles with unbalanced spin was very pronounced at this temperature, and at higher thermal treatment at 800 ºC the spectra show the contribution of Fe^{3+} and the Ag particles. The presences of iron in both series of samples are due to contamination by Ag particles from the electrode used during their respective production.

DISCUSSION RESULTS

Our results presented in this work show several interesting aspects in the SiO_2-Ag system with the incorporation of Ag particles in the starting solution. This system shows some significant differences with respect to other techniques for the Ag introduction. For example with Ag nitrates in sol-gel glasses [9,10,11,30] or with the introduction of Ag in melting glasses.

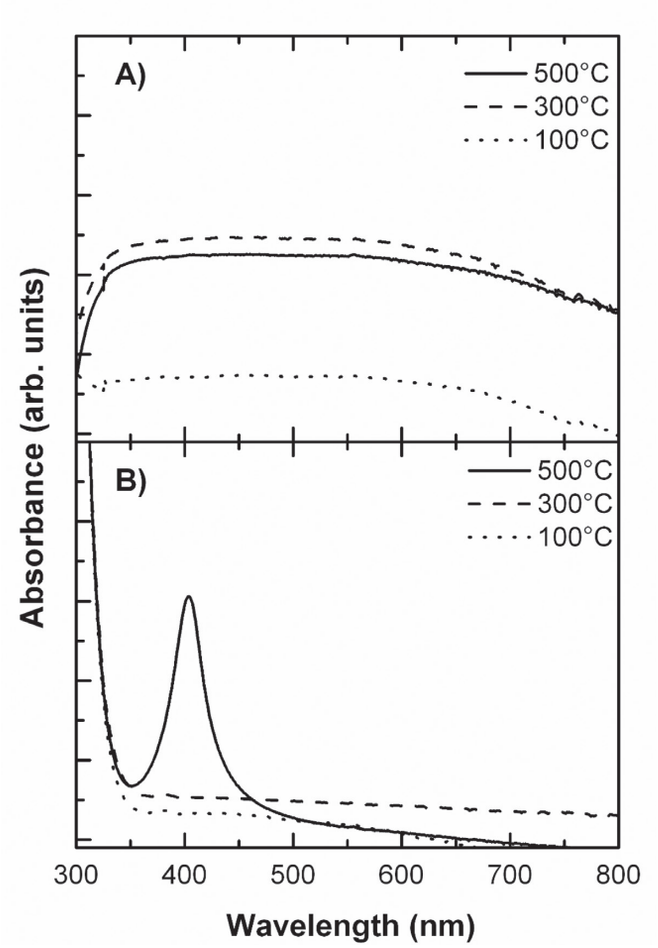

Fig.5. Shows absorption spectra of coating samples for B series.

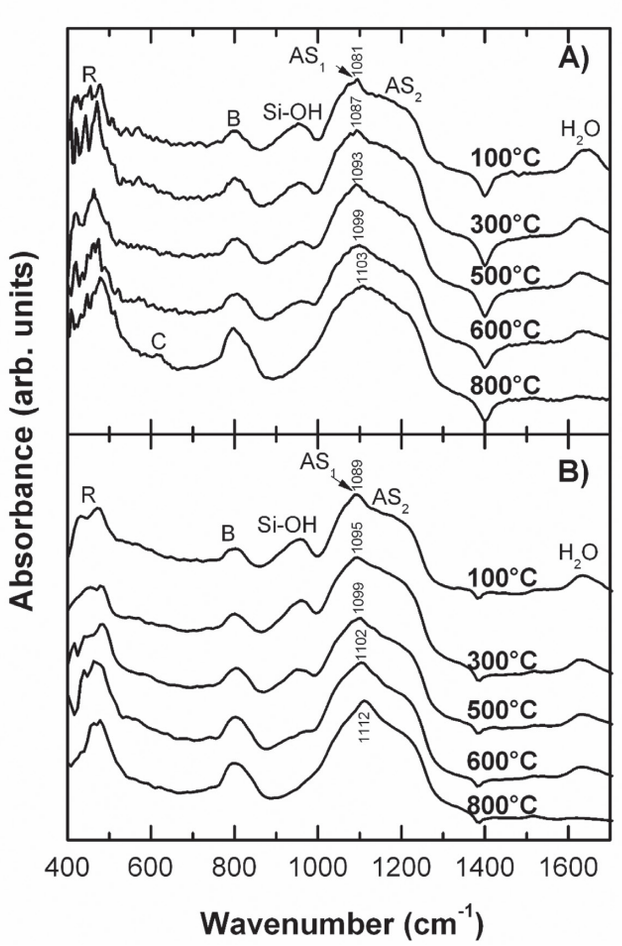

Fig. 6. Typical IR data, in the range of 400 to 1700 cm^{-1} for samples of A and B series as a function of the annealing temperature.

Structural changes in the SiO_2 matrix can be induced with the introduction of several kinds of particles, metallic and metallic oxides, such as Cu, Ag, Au [2,9,10,11], or in mixtures of SiO_2 with metallic oxides ($MgCO_3$, $CaCO_3$, Li_2CO_3,SrO, ZnO) and thermal annealing [8]. In sol-gel glasses with Ag introduction by nitrates in the starting solution and with a H_2O/TEOS ratio of 11.7 a crystallization process of the SiO_2 at annealing temperatures of 500 ºC with 4 %vol. of Ag, to the cristobalite phase was found. In a similar work [9,10,11,30] sol-gel glasses with the introduction of Ag and Cu particles by nitrates the transformation of the SiO_2 matrix to quartz and cristobalite phase at temperature annealing of 600 ºC [10] and 800 ºC was observed [29].

When SiO_2 glasses prepared by melting and with the thermal annealing in mixtures of SiO_2 and metallic oxides particles, it was found that the SiO_2 matrix can suffer a crystallization process to quartz phase at 700 ºC (with the introduction of $LiCO_3$) and cristobalite phase at 650 ºC (with the introduction of Na_2CO_3).

With these facts in mind, during this work the Ag particles were introduced in the starting solution to obtain coating samples and powders, submitted to a heat treatment from 100 to 500 ºC in the coating samples and 100 to 800 ºC in the powders samples.

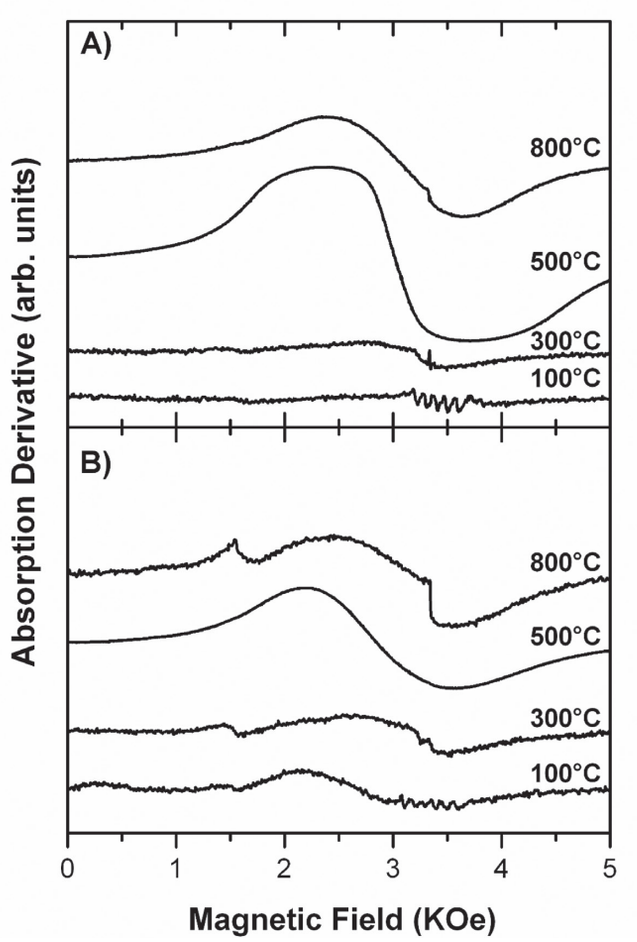

Fig. 7. Shows the EPR spectra evolution with the annealing temperature for series of samples A and B.

In the powder samples a crystallization process of the SiO_2 amorphous matrix to the cristobalite phase at 800 ºC with 0.7 %vol. of Ag was observed. With higher Ag concentrations the same crystallization process was found with higher efficiency in the phase transformation as well as an increase the Ag concentration. Unlike the crystallization process observed in samples with the introduction of Ag by nitrates, in this case the Ag concentration was lower but a higher annealing temperature is required (500 ºC in the nitrate case with 4 %vol. of Ag.) For both series of samples, Figs. 1 and 2, a more pronounced effect in the case of the samples A was observed. This crystallization process can be understood in accordance with the previous report [9,10,11] in two important aspects, a) it is the structure of the SiO_2 matrix which is determined by the relation H_2O/TEOS in the starting solution. b) Due to diffusion process of the Ag atoms in the growth and nucleation of Ag colloidal particles.

In this case, we are beginning with micrometric Ag particles in the starting solution; nevertheless the catalytic agent produces a dilution of these particles. Then, in the samples there are distribution sizes of Ag particles including atomic in some interstitial sites. With the thermal treatment these isolated Ag atoms diffuse to the nucleation centers and the interaction among the atoms and the lattice promoting the transformation of the amorphous SiO_2 matrix to the cristobalite phase. In Fig. 3, for both series of samples A) and B) the average size of the cristobalite particles was found to be 4 nm and in general the particle size of Ag is slightly lower with HNO_3 catalytic than with HCl.

The results shown in the Fig. 4 present an interesting evolution in the absorption spectra as a function of the thermal annealing. From the X-ray results, Figs 1 and 2, the presence of Ag particles in samples treated at 100 ºC were observed, However the absorption band due to Ag colloidal particles is only resolved for samples treated at 800 ºC for both series of samples. This fact indicates that there is a diffusion process which produces the growing of the Ag particles with suitable size, that contribute notably to the absorption spectra only at higher temperatures (800 ºC).

Based on this fact, it is indicated that the Ag particles present at lower annealing temperatures have a distribution size, that increases the background absorption but the characteristic colloidal band due to Ag with nanometric size and spherical shape is not resolved. Additional information from these spectra is related to an absorption band at around 320 nm which in turn is related with the presence of Fe^{3+} ions, these ions are due to contamination of the Ag particles during the production process [20].

Previous work of our group observed two necessary conditions for the transformation of the SiO_2 amorphous network to cristobalite phase [9,10,11]. First there is the conformation structure of the SiO_2 similar to the cristobalite phase which is obtained with higher ratios of H_2O/TEOS and the growing of colloidal Ag particles.

In this case it is worked with a sol-gel solution with higher ratio H_2O/TEOS, but differing from the previous work, in this case the structure show a higher retention capacity of silanol groups, up to temperatures of 600 ºC showing a pronounced effect in the HNO_3 catalytic agent case. Then, although we used the same solution point for introducing the Ag particles, in this case the structure of the SiO_2 network was slightly different than when the Ag by nitrates was introduced. These

differences in structure are evidenced by the IR absorption spectra, where is possible to identify the presence of OH groups up to temperatures of 600 ºC. This slightly structural difference combined with the reduction of the Ag atoms disposable for diffusion may be the explanation to obtaining higher temperatures of crystallization in this case. By means of the EPR results it was possible to identify the presence of the Fe^{3+} ions, whose spectra are well resolved for samples treated at 800 ºC. Symmetrical and broad absorption band centered around 3 KOe due to Ag particles is identified [31]. At higher annealing temperature the contribution of the Ag particles to the EPR spectrum was reduced and it is possible to resolve the Fe^{3+} ion structure with g factors of g=2.21 for series A) and g=2.31 for series B)

4. CONCLUSIONS

In this work two series of samples of Sol-gel glasses with incorporation of Ag particles at the starting solution were analyzed. The samples were prepared as both coating and in powder forms.

The introduction of the Ag particles in the SiO_2 matrix induces a crystallization process to cristobalite phase of the SiO_2 with the annealing treatment, this phase was observed at 800 ºC with 0.7 %vol. of Ag, for higher Ag concentration the same crystallization process at the same temperature is observed.

The structure of the SiO_2 network with the introduction of the Ag particles shows itself as being more open than in the case when the introduction of Ag is by nitrates, showing the presence of some defect points such as silanol groups and O_2^-.

The EPR spectra show the presence of Ag particles and Fe^{3+} ions, because of this spectra it is concluded that the Ag is not in the form of ions, nevertheless, for the prepared samples without annealing treatment there are some Ag atoms dispersed in the SiO_2 matrix, which diffuse to the nucleation Ag particles, and this diffusion process is the mechanism responsible for inducing the crystallization process.

For both series of samples the grain size of the cristobalite phase is around 16 nm for thermal treatment at around 800 ºC.

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